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(54) Title of Invention: PROCESS FOR PRODUCTION OF α -OLEFIN
TYPE RANDOM COPOLYMERS

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SPECIFICATION

1. Title of the Invention

Process for production of α -olefin type random copolymers

RAPIDO TECHNICAL TRANSLATIONS, INC.
LSBD 14 December 1992

2. Patent Claim, Scope of

Process for production of α -olefin type random copolymers, characterized by the fact that copolymers having an α -olefin component content of 30 to 99 mole% are obtained by conducting the copolymerization of a C_{2-3} - α -olefin and ethylene in the presence of catalysts which are formed from

(A) compounds of periodic table group IVB transition metals having as ligands multisite coordination compounds in which at least two kinds of groups which are selected from the group consisting of indenyl groups, substituted indenyl groups, and their partial hydrogenation products are bonded through the medium of lower alkyl groups and

(B) aluminoxanes.

3. Detailed Description of the Invention

(Profitable Use Sectors from the Industrial Standpoint)

The present invention relates to a process for production of novel α -olefin type random copolymers; more particularly it relates to a process for production of modifiers for use in thermoplastic resins which have an excellent effect in improving the heat sealability and impact resistance, particularly the impact resistance at low temperatures, by means of blending into the thermoplastic resins α -olefin type random copolymers having narrow molecular weight distributions and having excellent transparency, surface nontackiness, and tensile and other properties, for example α -olefin type random

copolymers and other olefin type polymers and so forth which are suitable for forming films for packaging use, sheet products, and other melt-molded products which have excellent transparency, antiblocking characteristics, and so forth.

(Prior Art)

In the past, use of vinyl chloride resins in molding application fields for soft or semihard resins was predominant, but because of problems such as generation of corrosive gases at the time of waste product incineration and concepts about safety in respect to residual monomers and plasticizers, conversion over to olefin type soft or semihard resins came to be desired. Consequently, demands increasingly grew larger for α -olefin type soft copolymers for use in the molding field or for applications such as modifiers for use in various kinds of resins.

Where more than two kinds of α -olefin copolymers are commonly known for the said α -olefin type soft copolymers, as processes for the production of them, processes have been known for copolymerizing two or more kinds in the presence of a titanium type catalyst consisting of a titanium compound and an organoaluminum compound or a vanadium type catalyst consisting of a vanadium compound and an organoaluminum compound. The α -olefin type soft copolymers obtained with the titanium type catalysts were generally inferior in random copolymerizability, had broad molecular weight distributions and composition distributions, and were inferior in trans-

parency, surface nontackiness, and dynamic properties. Moreover, α -olefin type soft copolymers obtained with the vanadium type catalysts generally had greater than 50 mole% ethylene content; by comparison with the copolymer obtained with the titanium type catalysts, randomness was improved; the molecular weight distribution and composition distribution were narrowed; and the transparency, surface nontackiness, and dynamic properties were considerably improved, but their performance was unsatisfactory in strictly (?) demanding applications, and α -olefin type copolymers with performances more improved than these were demanded.

Quite recently, as olefin type resins like these which have been used in molding application fields for soft or semi-hard resins, there have been olefin type copolymers such as ethylene type copolymers, propylene type copolymers, and 1-butene type copolymers. Among these olefin type soft or semi-hard resins, as relates to the soft 1-butene type random copolymers which are formed from 1-butene and propylene with 1-butene taken as the main component, there have been a large number of proposals. Among them, 1-butene type random copolymers have been disclosed which are produced by employing titanium trichloride and titanium tetrachloride type catalysts in U.S. Patent Specification No. 3,278,504, U.S. Patent Specification No. 3,332,921, U.S. Patent Specification No. 4,168,361, and Brit. Patent Specification No. 1,018,341. However, because

things shared in common by these 1-butene type random copolymers were a considerable content of low molecular weight components such as a fraction soluble in boiling methyl acetate and a fraction soluble in an acetone-n-decane mixed solvent (1/1 volume ratio) as well as a broad composition distribution and molecular weight distribution, as concerns molded materials formed from these 1-butene type random copolymers, especially films, sheets, and so forth, surface tackiness was considerable and blocking was appreciable. And since the randomness of almost all of the materials was low and the transparency was inferior, molded products having high commercial value were not obtained.

In the aforementioned U.S. Patent Specification No. 3,278,504 propylene-1-butene copolymers having a 1-butene content of 30 to 70 mole% were proposed. It was disclosed that the said 1-butene copolymers were produced by using titanium tetrachloride and titanium trichloride, but in the copolymers produced with catalyst systems like these the content of the fraction soluble in boiling methyl acetate exceeded 2 wt%, and moreover the content of the fraction soluble in the acetone-n-decane mixed solvent (1/1 volume ratio) was considerable; they had surface tackiness, and were soft resins inferior in transparency.

Also in the aforementioned U.S. Patent Specification No. 3,332,921 and Brit. Patent Specification No. 1,084,953 various kinds of 1-butene type copolymers differing in 1-butene content were proposed which were produced by employing titanium

trichloride catalysts, but among these copolymers, the 1-butene type copolymers having 60-99 mole% 1-butene content had the same properties as the 1-butene type copolymers in the proposal of the aforementioned U.S. Patent Specification No. 3,278,504.

Furthermore, according to the aforementioned Brit. Patent Specification No. 1,018,341, copolymers having 25 to 90 mole% 1-butene content were obtained by jointly using a transition metal halide such as titanium trichloride and a phosphoric acid derivative. Among the copolymers concretely disclosed in this proposal, if seen as relating to the 1-butene type copolymers having 50 to 90 mole% for the 1-butene content, only materials having greater than 1.5 wt% for the acetone soluble fraction were disclosed. According to the studies of the present inventors, it was discovered that the content of the fraction of these copolymers soluble in boiling methyl acetate was much more, exceeding 2 wt%, also that the content of the fraction soluble in the acetone-n-decane mixed solvent (1/1 volume ratio) was considerable, exceeding $5 \times [\eta]^{-1.2}$ wt%, and that only molded products having considerable surface tackiness and inferior in transparency could be obtained from the said 1-butene type copolymers.

Still further, propylene-1-butene copolymers having a propylene content in the range of 40 to 90 mole% were disclosed in the aforementioned U.S. Patent Specification No. 4,168,361, but among these copolymers, as relates to the copolymers having a 1-butene content of 50 to 60 mole%, the

same as above, according to the studies of the present inventors, only molded products could be obtained in which the content of the fraction soluble in acetone-n-decane was large, the surface tackiness from the said 1-butene type copolymers was considerable, and the transparency was inferior.

On the other hand, a process was proposed in JP Tokkai No. Sho 50-38787 Koho for obtaining random copolymers of no quality by conducting the polymerization at high temperatures and employing a titanium chloride system catalyst.

As concerns these processes, according to studies of the present inventors, the methyl acetate-soluble fraction was considerable; they were inferior as relates to tensile properties; and they could not be used for resin applications.

In addition, in JP Tokkai No. Sho 54-85293 the present applicant proposed 1-butene-propylene random copolymers with 1-butene taken as the main component which had a narrow composition distribution, little of the fraction soluble in boiling methyl acetate, and small surface tackiness. Nevertheless, it was clear that the content of low molecular weight components in the 1-butene-propylene copolymers which were offered on the basis of this proposal, especially the content of the low molecular weight polymer which was represented in the fraction soluble in boiling methyl acetate and the surface tackiness of the molded products formed from the said copolymers were considerably improved by comparison with previous materials, but shortcomings existed in that the molecu-

lar weight distribution (M_w/M_n) of the said 1-butene type random copolymers was 3.6 and was not sufficiently narrow; the content of the low molecular weight polymer components in the copolymer, which was represented by the fraction soluble in acetone-n-decane (1/1 volume ratio), and the surface tackiness with elapsed time for resin composition molded products for example films in which the said 1-butene-propylene random copolymer had been blended into a polypropylene resin for the purpose of improving impact resistance was easily increased; it was difficult to say that they were yet satisfactory for applications in fields where performance in surface nontackiness, transparency, and so forth was required in high degree. And the said 1-butene-propylene random copolymers further based on this proposal had low crystallinity, but they were inferior in dynamic properties such as rigidity and were still unsatisfactory for applications in fields where these dynamic properties were required in high degree.

On the other hand, as new Ziegler type olefin polymerization catalysts which differ from the titanium type catalysts or vanadium type catalysts known from the past, catalysts formed from zirconium compounds and aluminoxanes have been proposed thus far in JP Tokkai No. Sho 58-19309 Koho, Tokkai No. Sho 59-952925 Koho, Tokkai No. Sho 60-35005 Koho, Tokkai No. Sho 60-35006 Koho, Tokkai No. Sho 60-35007 Koho, and Tokkai No. Sho 60-35009. In the prior art literature on them,

where more than two kinds of α -olefin copolymers have been disclosed, for example in Practicable Example 7 of JP Tokkai No. Sho 58-19309 Koho, in Practicable Example 1 - Practicable Example 3 of JP Tokkai No. Sho 60-35006 Koho, and in Practicable Example 10 and Practicable Example 11 of JP Tokkai No. Sho 60-35007 Koho, ethylene- α -olefin copolymers having respective α -olefin contents of 3-43 mole% are disclosed, but in many cases anyhow these ethylene- α -olefin copolymers had broad molecular weight distributions and composition distributions or performance such as transparency, surface nontackiness, and dynamic properties or performance as modifiers for thermoplastic resins which were unsatisfactory for applications in profitable use sectors; furthermore, α -olefin type soft copolymers in which these qualities were improved were greatly demanded.

In addition, as relates to soft low-crystallinity propylene type copolymers containing a propylene component, due to copolymerizing propylene with α -olefins other than propylene, proposals were made by the present applicant in JP Tokkai No. Sho 52-19153 Koho, Tokkai No. Sho 55-118909 Koho, Tokkai No. Sho 55-118910 Koho, Tokkai No. Sho 53-79984 Koho, Tokkai No. Sho 53-104686 Koho, Tokkai No. Sho 54-85293 Koho, Tokkai No. Sho 60-38414, and so forth. By comparison with the soft low-crystallinity propylene type copolymers known from the past these soft low crystallinity propylene type copolymers had a reduced content of the fraction soluble in boiling methyl

acetate and had improved surface nontackiness, blocking characteristics, and transparency, but it was difficult to speak about them being satisfactory for applications in fields where these qualities were more strictly demanded. Furthermore, the copolymers obtained in these processes had broad molecular weight distributions anyhow, and as relates to the point of dynamic properties for applications in fields where these qualities were strictly demanded, furthermore soft low-crystallinity propylene type copolymers in which the aforementioned qualities were more excellent were greatly demanded. (Problem Points Regarded as Solved by the Invention)

The present inventors observed (?) that the prior α -olefin type random copolymers had broad molecular weight distributions and composition distributions and had a considerable content of low molecular weight polymer and that molded materials obtained from the said α -olefin type random copolymers were inferior in surface nontackiness, transparency, and dynamic properties such as rigidity and conducted development research for the purpose of offering α -olefin type random copolymers in which these properties were improved by comparison with prior α -olefin type random copolymers.

As a result of that, the present inventors discovered that α -olefin type random copolymers not disclosed in the previously known literature could exist which were α -olefin type random copolymers which were formed from a C_{23} - α -olefin and an ethylene component and which combined the property values defined in later descriptions (A) to (I), and they succeeded in synthesizing them.

Furthermore, they discovered that as compared with the previously known α -olefin type random copolymers, these novel α -olefin type random copolymers had narrow molecular weight distributions and composition distributions and had little content of fractions of low molecular weight polymer components, particularly little content of fractions of low molecular weight components which are represented by both the fraction soluble in boiling methyl acetate and the fraction soluble in acetone-n-decane mixed solvent (1/1 volume ratio), and they discovered that molded materials obtained from the said α -olefin type random copolymers had excellent surface nontackiness, transparency, and dynamic properties such as rigidity.

Consequently, the object of the present invention was that of offering a process for production of novel α -olefin type random copolymers which are formed from a $C_{\geq 3}$ - α -olefin component and an ethylene component.

Furthermore, another object of the present invention was that of offering a process for production of modifiers for use in thermoplastic resins which are excellent in improvement effects on heat sealability or impact resistance, especially low temperature impact resistance in dependence on blending them into thermoplastic resins such as olefin type polymers obtained by means of processes other than the process of the present invention.

This is made clear anyhow by means of the following disclosure of the advantages of the above described objectives side by side with many other further objectives of the present invention.

(Measures and Operations for Solving Problem Points).

According to the present invention, a process is offered for the production of α -olefin type random copolymers, characterized by the fact that copolymers having an α -olefin component content of 30-99 mole% are obtained by conducting the copolymerization of a C_{23} - α -olefin and ethylene in the presence of catalysts which are formed from

(A) compounds of periodic table group IVB transition metals having as ligands multisite coordination compounds in which at least two kinds of groups which are selected from the group consisting of indenyl groups, substituted indenyl groups, and their partial hydrogenation products are bonded through the medium of lower alkyl groups and

(B) aluminoxanes,

and the process is offered for the production of modifiers for use in thermoplastic resins which consist of the said α -olefin type random copolymers.

According to the above described production process, α -olefin type random copolymers are obtained, and modifiers consisting of the said α -olefin type random copolymers for use in thermoplastic resins are obtained, characterized by the fact that they are α -olefin type random copolymers formed from a C_{23} - α -olefin and ethylene;

- (A) their compositions are in the range of 30 to 99 mole% for the C_{23} - α -olefin component and 1 to 70 mole% for the ethylene component;
- (B) the limiting viscosities $[\eta]$ measured at 135 °C in decalin are in the range of 0.5 to 6 dL/g;
- (C) the molecular weight distributions (M_w/M_n) measured by gel permeation chromatography (GPC) are in the ≤ 3 range;
- (D) the melting point. (T_m) measured by means of differential scanning calorimetry is in the range of 30 to 140 °C;
- (E) the degree of crystallization measured by means of an x-ray diffraction method is in the range of 0.5 to 60%;
- (F) the weight of the fraction (W_1 wt%) soluble in boiling methyl acetate is in the 1 wt% range;
- (G) the weight of the fraction (W_2 wt%) soluble at 10 °C in acetone-n-decane mixed solvent (1/1 volume ratio) is in the range of $\leq 4 \times (\eta)^{-1.2}$ wt%;
- (H) the $\alpha\beta$ and $\beta\gamma$ signals attributable to methylene chains between two tertiary carbon atoms which are adjacent in the copolymer main chain in the ^{13}C -NMR spectra of the copolymers are not observed;
- (I) the value which is expressed by general Equation (I)

$$B = \frac{P_{OE}}{2P_O : P_E} \quad (I)$$

is in the range of general Equation (II)

$$1.00 \leq B \leq 2 \quad (II)$$

(in the equation P_O indicates the mole percent content of the α -olefin component in the copolymer; P_E indicates the mole percent content of the ethylene component; P_{OE} indicates the

mole percent of α -olefin-ethylene chains in the total dyad chains).

In the α -olefin type random copolymers obtained by the process of the present invention (the ones which are called the α -olefin type random copolymers of the present invention), as concerns the composition (A) of the said copolymers, the ethylene component is in the range of 1 to 70 mole%, desirably 1 to 65 mole%, and the α -olefin component content is in the range of 30 to 99 mole%, desirably 35 to 99 mole%. Moreover, in cases where the said copolymer is a copolymer of propylene and ethylene, the content of ethylene is in the range of 10 to 70 mole%, desirably 20 to 65 mole%; in cases where it is a copolymer of 1-butene and ethylene, the content of ethylene is in the range of 1 to 50 mole%, desirably 1 to 40 mole%. If the content of the α -olefin component in the said copolymer is smaller than 30 mole% and if the content of the ethylene component is larger than 70 mole%, the transparency of the said copolymer turns out to be lowered. Also if the content of the α -olefin component becomes larger than 99 mole% and if the content of the ethylene component becomes smaller than 1 mole%, the distinctive characteristics of the soft copolymers are lost due to the transparency and impact resistance being lowered. Also, in cases where the said α -olefin component is a 1-butene component, the transition of the said copolymers from type II crystals to type I crystals

becomes slow; along with changes with elapsed time in the properties of the molded products becoming greater, the transparency becomes inferior. Herewith, the α -olefin component units are C_{3-20} - α -olefins, desirably C_{3-18} - α -olefins, especially desirably C_{3-12} - α -olefins; there is no objection (?) to having one component or a mixture of two or more components. Concretely, as α -olefin component units such as these, propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-decene, 1-tetradecene, 1-octadecene, and others can be illustrative.

The limiting viscosity (η) (B) measured in decalin at 135°C for the α -olefin type random copolymers which are obtained by the process of the present invention is in the range of 0.5 to 6 dL/g, desirably 1 to 5 dL/g. These values are measures which indicate the molecular weight of the α -olefin type random copolymers which are obtained by the process of the present invention; lumped together with other property values, the aforementioned excellent qualities were laid down anyhow for being imparted to random copolymers.

The molecular weight distribution (\bar{M}_w/\bar{M}_n) (C) found by gel permeation chromatography (GPC) for the α -olefin type random copolymers which were obtained by the process of the present invention is in the range ≤ 3 , desirably ≤ 2.8 , especially desirably ≤ 2.5 . Since the \bar{M}_w/\bar{M}_n values for the α -olefin type random copolymers which had been proposed in the past were ≥ 3 ,

the molecular weight distributions were termed not sufficiently narrow; when low molecular weight polymer components were intermixed, the surface nontackiness was inferior on that account and became the root cause for blocking. These property values for the α -olefin type random copolymers which were obtained by the process of the present invention lumped together with other property values were imparted to the copolymers the aforementioned excellent qualities. Still further, the measurements of \bar{M}_w/\bar{M}_n values were performed as follows according to the military information monthly operations publication, "Gel Permeation Chromatography".

(1) The molecular weight M and the GPC (Gel Permeation Chromatograph) count were measured by using polystyrene of known standard molecular weight (Toyo Soda brand Standard Dispersion Polystyrene); correlation comparison normal curves were prepared for molecular weight M and EV (Elution Volume). This time the concentration was taken as 0.02 wt%.

(2) Samples for the GPC chromatograph by way of GPC measurements were taken. The value of \bar{M}_w/\bar{M}_n was found by calculating the polystyrene-converted number average molecular weight \bar{M}_n and weight average molecular weight \bar{M}_w in dependence on the aforementioned (1). The sample preparation conditions and GPC measurement conditions at the time were as follows.

(Sample Preparation)

(1) The samples were apportioned in conical flasks along with *o*-dichlorobenzene solvent so as to arrive at 0.1 wt%.

(a) 0.05 wt% in respect to the polymer solution of the age resistor 2,6-di-tert-butyl-p-cresol was added to the conical flask in which the sample had been placed.

(b) The temperature of the conical flask was raised to 140 °C; stirring was conducted for about 30 min; and they were dissolved.

(c) The filtrate went off to GPC.

(GPC Measurement Conditions)

The following conditions came into effect.

- | | |
|-------------------|-------------------------------------|
| (1) Apparatus | Waters company make (150-C-ALC/GPC) |
| (2) Column | Toyo Soda make (GMH type) |
| (3) Sample volume | 400 μ L |
| (4) Temperature | 140 °C |
| (5) Flow rate | 1 mL/min |

The melting points (D) which were measured by means of a differential scanning calorimeter (they are abbreviated below as DSC melting points) for the α -olefin type random copolymers which had been obtained by the process of the present invention were in the range of 30 to 140 °C, desirably 40 to 120 °C. Existence of the said DSC melting points is a measure which indicates that they are copolymers possessing crystallinity which distinguishes them from the previous noncrystalline α -olefin type random copolymers; lumped together with other property values the aforementioned excellent qualities were laid down to be imparted to the copolymers. Herewith, the DSC melting points were the maximal endothermic

peak temperatures (T_m) obtained when approximately 5 mg samples were inserted into the sample measurement case and measurements were made as far as 20-200 °C with a temperature rise rate of 10 °C/min (still further, in the case of the 1-butene type random copolymers, pressed sheets after at least 20 h elapsed time in a molding machine were used).

The degree of crystallization (Σ) measured by means of an x-ray diffraction method for the α -olefin type random copolymers which were obtained by the process of the present invention was in the range of 0.5 to 60%, desirably 0.5 to 55%. These property values were measures which indicated that the α -olefin type random copolymers which were obtained by the process of the present invention were excellent in tensile properties; lumped with other property values, the aforementioned excellent qualities were laid down for being imparted to the random copolymers. Further still, the degree of crystallization of the 1-butene type random copolymers was found by means of x-ray diffraction measurements on pressed sheets after at least 20 h elapsed time in a molding machine.

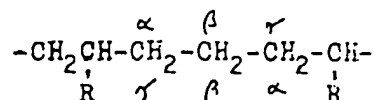
The weight of the fraction soluble in boiling methyl acetate (W_1 wt%) (F) for the α -olefin type random copolymers which were obtained by the process of the present invention was in a range ≤ 1 wt%, desirably 0.001-0.5 wt%, especially desirably 0.003-0.2 wt%. These property values were measures which indicated the content of the low molecular weight poly-

mer component in the α -olefin type random copolymers which were obtained by the process of the present invention and indicated the breadth of the composition distribution and molecular weight distribution for the said copolymers; the α -olefin type random copolymers which were proposed in the past had a considerable weight of the said fraction soluble in boiling methyl acetate and were inferior in surface non-tackiness, which became the root cause for much blocking. These property values for the α -olefin type random copolymers which had been obtained by the process of the present invention lumped with other property values were laid down as aforementioned excellent qualities for imparting to the copolymers. The weight of the said fraction soluble in boiling methyl acetate was measured by the following method. Namely, 1 mm X 1 mm X 1 mm size sample pieces were placed in a cylindrical glass filter; they were extracted for 7 h with a Soxhlet extractor with a degree of reflux of 1 cycle/5 min; the weight of the extraction residue was found by drying it until constant weight in a vacuum dryer (degree of vacuum ≤ 10 mm Hg); the weight (W_1) of the fraction soluble in boiling methyl acetate was found by difference in weight from that of the original sample, as the percentage for the weight of the said fraction soluble in boiling methyl acetate referred to the weight of the original sample. The weight (W_2 wt%) (C) of the fraction soluble in acetone-n-decane mixed solvent (1/1 volume ratio) at 10 °C for the α -olefin type random copolymers

which had been obtained by the process of the present invention based on the weight of the said copolymer was in the range of $\leq 4 \times (\eta)^{-1.2}$ wt%, desirably $0.05 \times (\eta)^{-1.2}$ to $3.5 \times (\eta)^{-1.2}$ wt%, especially desirably $0.1 \times (\eta)^{-1.2}$ to $3 \times (\eta)^{-1.2}$ wt% (here, (η) indicates the numerical value of the limiting viscosity of the said copolymer values exclusive of dimensions). These property values were measured which indicated the content of the fraction of the low molecular weight polymer component in the α -olefin type random copolymers which were obtained by the process of the present invention and indicated the breadth of the composition distribution and molecular weight distribution of the said copolymer. The α -olefin type random copolymers known from the past had much of the fraction soluble in the said acetone-n-decane mixed solvent, were inferior in surface nontackiness, and were the root cause of much blocking. These property values for the α -olefin type random copolymers which had been obtained by the process of the present invention lumped with other property values laid down the aforementioned excellent qualities for being imparted to the copolymers. The measurement determinations for the weight of the said copolymer fraction soluble in the mixed solvent were made according to the following method. Namely, 1 g of copolymer sample, 0.05 g of 2,6-di-tert-butyl-4-methylphenol, and 50 mL of n-decane were introduced into a 150 mL flask furnished with a blade stirrer, and they were dissolved on a 120 °C oil bath. After dissolving, radiative cooling down took place naturally at air temperature for 30 min; then

50 mL of acetone was added in 30 s; it was cooled for 60 min on a 10 °C water bath. The precipitated polymer and the solution in which the low molecular weight polymer component was dissolved were filtered and separated with a glass filter; the solution was dried until coming to constant weight at 10 mm Hg and 150 °C, and the weight was measured. The weight of the copolymer fraction soluble in the aforementioned mixed solvent was calculated and determined as the percentage referred to the weight of the sample copolymer. Still further, in the aforementioned measurement method, stirring was carried out continuously from the time of dissolving until just before filtration.

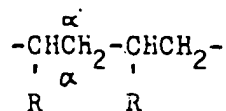
If seen in respect to the arrangement state of the ethylene component and α -olefin component (H), the $\alpha\beta$ and $\beta\gamma$ signals attributable to methylene chains between two tertiary carbon atoms which are adjacent in the main chain of the copolymer in the ^{13}C -NMR spectra of the said copolymers are not observed. This is described more concretely; in the copolymer of ethylene and the α -olefin ($\text{CH}_2=\text{CH}-\text{R}$, R an ethyl group) the following bonds:



if seen from the tertiary carbon on the left side derived from the α -olefin, the three methylene groups in the center are in α , β , and γ positions from the left side; on the other hand if seen from the tertiary carbon on the right side, they are

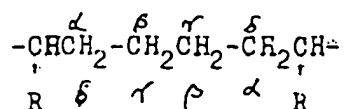
in the α , β , and γ positions from the right side. For that reason, in the above mentioned bond units, there were methylene groups which gave $\alpha\gamma$ and $\beta\beta$ signals, but there were no methylene groups which gave $\alpha\beta$ and $\beta\gamma$ signals.

On the other hand, in the following bonds:

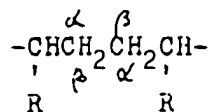


which were bonded with oppositely facing α -olefin pairs, only methylene groups which gave $\alpha\alpha$ signals were present; there were no methylene groups which gave $\alpha\beta$ and $\beta\gamma$ signals.

On the other hand, the following bonds



and



possess methylene groups which gave respectively a $\beta\gamma$ signal and an $\alpha\beta$ signal.

As is clear from the above description, it was found that the directions of the ethylene and α -olefin bonds in the α -olefin bonds in the α -olefin type random copolymers which had been obtained by means of the process of the present invention were observable. These specifics about the α -olefin type random copolymers were things which indicated the arrangement state of the ethylene components and α -olefin components of which the copolymer was composed; lumped with other pro-

perty values excellent qualities such as the above mentioned were laid out for imparting to the copolymers.

As concerns the α -olefin type copolymers of the present invention, the B values which are expressed by the following Equation (I)

$$B = \frac{P_{OE}}{2P_O \cdot P_E} \quad (I)$$

are in a range which satisfies the following Equation (II)

$$1.00 \leq B \leq 2 \quad (II)$$

(in the equation P_E indicates the mole% content of the ethylene component in the copolymer; P_O indicates the mole% content of the α -olefin component; and P_{OE} indicates the mole percent content of α -olefin-ethylene chains in the total dyad chains). Furthermore, the B values for the α -olefin type random copolymers which are obtained by the process of the present invention are found in correlations with the mole percent contents of the ethylene component in the copolymer, desirably in correlations such as the following.

In cases where the ethylene content in the copolymers is ≤ 50 mole%, it is in a range which satisfies

$$1.0 + 0.3 \times P_E \leq B \leq 1/(1-P_E),$$

more desirably, the general formula

$$1.0 + 0.4 \times P_E \leq B \leq 1/(1-P_E),$$

especially desirably, the general formula

$$1.0 + 0.5 \times P_E \leq B \leq 1/(1-P_E), \text{ and}$$

in cases where the ethylene content in the copolymer is ≥ 50 mole%, it is in a range which satisfies

$$1.3 - 0.3 \times P_E \leq B \leq 1/P_E.$$

more desirably, the general formula

$$1.4 - 0.4 \times P_E \leq B \leq 1/P_E,$$

especially desirably, the general formula

$$1.5 - 0.5 \times P_E \leq B \leq 1/P_E.$$

In the α -olefin type random copolymers which are obtained in the process of the present invention the property values resulting from these B values are indexes which indicate the state of distribution of each monomer component in the copolymer chain; the larger the B values are, the fewer the block chains are; when the distribution of the ethylene component and α -olefin component become uniform, the randomness is excellent, and when the existence of a copolymer with a narrow composition distribution is indicated, lumped together with other property values excellent qualities such as the above mentioned are laid down for being offered in the copolymers.

B values were calculated from the respective calculated component contents P_E , P_O , and P_{OE} according to the reports of G.J. Ray (Macromolecules 10, 773(1977)), J.C. Randall (Macromolecules 15, 353(1982)), and others. P_E , P_O , and P_{OE} were found from ^{13}C -NMR spectral measurements for the said copolymer samples. Namely, ^{13}C -NMR spectra were measured for samples in which about 200 mg of copolymer had been dissolved in 1 mL of hexachlorobutadiene in a 10 mm ϕ test tube, ordinarily under the measurement conditions of a measurement temperature of 120 °C, a measurement frequency of 25.05 MHz, a spectral width of 1500 Hz, a filter width of 1500 Hz, a pulse

repeat time of 4.2 sec, a pulse width of 7 μ sec, and a number of accumulated cycles of 2000-5000 cycles; from these spectra P_E , P_O , and P_{OE} were found.

The property values specified in the above discussed (A) to (I) for the α -olefin type random copolymers which were obtained by the process of the present invention were satisfactory. Besides the specific values for the above described (A) to (I) for the more desirable α -olefin type random copolymers which were obtained by the process of the present invention, property values for at least one of the following (J) to (R) were satisfactory.

Stress at the breaking point (J_1) measured according to the method of JIS K6301 for the α -olefin type random copolymers which were obtained by the process of the present invention was in the range of 3 to 1000 kg/cm^2 , desirably 5 to 800 kg/cm^2 ; elongation at the breaking point (K_1) measured according to the method of JIS K6301 was in the range $\geq 300\%$, desirably 500 to 1500%. The property values for the above mentioned stress at the breaking point (J_1) and elongation at the breaking point (K_1) were measured according to JIS K6301 tensile test methods. Namely, ring test specimens with an inside diameter of 18 mm and an outside diameter of 22 mm which had been punched from 1 mm thick pressed sheets molded according to JIS K6758 were used; measurements were made at an extension rate of 500 mm/min in the atmosphere at 25 $^{\circ}\text{C}$.

Furthermore, haze (N) which was measured for the α -olefin type random copolymers of the present invention according to JIS K6714 on 1 mm thick sheets molded according to JIS K6758 was in the range of $\leq 30\%$, desirably $\leq 20\%$.

In cases where the α -olefin type random copolymers which were obtained by the process of the present invention were 1-butene type random copolymers which were obtained by means of copolymerization of a 1-butene component and an ethylene component, (J_1), (K_1), and at least one of the (N) to (Q) property values were satisfactory. Namely, the shear stress at the yield point (N) measured according to the method of JIS K7113 was in the range of 1 to 200 kg/cm², desirably 2 to 180 kg/cm²; the stress at the breaking point (J_1) measured according to the method of JIS 7113 was in the range of 3 to 1000 kg/cm², desirably 5 to 800 kg/cm², and the elongation at the breaking point (K_1) measured according to the method of JIS K7113 was in the range $\geq 300\%$, desirably 350 to 1000%.

In the present invention the property values for the above described shear stress at the yield point (N), stress at the breaking point (J_1), and elongation at the breaking point (K_1) were measured according to the JIS K7113 tensile test method. Namely, test specimens formed by JIS K7113 No. 2, punched 19 h after molding from 1 mm thick pressed sheets which had been molded according to JIS K6758 for samples were used; measurements were made 20 h after molding the above mentioned pressed sheets at an extension rate of 50 mmg/min in the atmosphere

at 25 °C. In cases where no yield point in shear distinctly appeared, the stress at 20% elongation was taken as the shear stress at the yield point.

And in cases where the α -olefin type random copolymers were 1-butene type random copolymers which were obtained by means of copolymerization of 1-butene with ethylene, the torsional rigidity modulus (G) measured according to the method of JIS K6745 for the said 1-butene type random copolymers was for example in the range of 5 to 3000 kg/cm², desirably 10 to 200 kg/cm². As the method for measurement of the torsional rigidity modulus, narrow test specimens 64 mm in length and 635 mm in width (words length and width reversed?) punched 9 days after molding from 1 mm thick pressed sheets which had been molded according to JIS K6758 were used; 10 days after molding the pressed sheets the values were measured 5 sec after positioning (?) at an angle of 50 to 60° in the atmosphere at 25 °C.

Young's modulus (P) measured according to the method of JIS K7113 for the said 1-butene type random copolymers was for example in the range of 10 to 5000 kg/cm², desirably 20 to 4000 kg/cm². And Young's modulus (P) for the said 1-butene type random copolymers was expressed desirably in correlation with the mole% content b of the ethylene component by way of the general equation

$$5000 \times 10^{-(b/25)} \geq K \geq 2000 \times 10^{-(b/15)}$$

Measurements of Young's modulus were performed according to the same tensile test methods as for the measurement of the aforementioned (J_1), (K_1), and (N).

In cases where the α -olefin type random copolymers which were obtained by the process of the present invention were 1-butene type random copolymers which were obtained by means of copolymerization of 1-butene and ethylene, since the crystal transition for the said 1-butene type random copolymers proceeds rapidly by comparison with that of the 1-butene homopolymer, it is characteristic that changes with elapsed time in the properties are small. By contrast with this, for example three kinds of crystal types (Type I, Type II, and Type III) exist for the 1-butene homopolymer; as it is known that the crystal transition occurs in correlation with changes in temperature and time, since especially below ambient (?) temperature the transition from the metastable Type II crystal morphology is slow, as relates to applications to actual molded products, shortcomings existed involving various difficulties such as deformation and property changes with elapsed time in molded products.

The standard deviation values σ (Q) for the content of the α -olefin component in the said α -olefin type random copolymers were for example $\leq 0.4a$ mole%, desirably $\leq 0.2a$ mole% (in the formula a indicates the mole% content of the ethylene component in the said α -olefin type random copolymers). The said standard deviation values σ were measures which indicated

the randomness of the said α -olefin type random copolymers; adding to the aforementioned property values (A) to (F), still further, copolymers for which the property value (Q) was satisfactory exhibited more excellent properties. The standard deviation values σ for the α -olefin type random copolymers of the present invention were computed and determined according to the following formula on the basis of the composition distribution for the said copolymer. Further still, the composition distributions for the said copolymers were measured by means of an extraction column separation method with p-xylene solvent by changing the extraction temperature by steps of 5 °C each from 0 to 130 °C. This time 2 L of p-xylene in respect to 10 g of copolymer sample was used for the extraction at constant temperature; the extraction was conducted for 4 h.

$$\sigma = \left[\int_0^{100} (\bar{x} - x)^2 f(x) dx \right]^{\frac{1}{2}}$$

Herein, \bar{x} indicates the average content (mole%) of the α -olefin in the copolymer; x indicates the α -olefin content (mole%); $f(x)$ indicates the differential weight percent of the component having a quantity x (mole%) of α -olefin content.

In cases where the α -olefin type random copolymer in the present invention was a propylene type random copolymer which had been obtained by copolymerization of propylene and ethylene, the microisotacticity (R) seen in the said propylene type

random copolymers (three-propylene chains) was ≥ 0.8 , desirably ≥ 0.9 . Among the propylene chains in the copolymer chains of the propylene type random copolymers of the present invention the ratio (y/x) indicates the number y of the above mentioned three kinds of arrangements which can be assumed by three-propylene chains relative to the total number x out of the possible number of combinations of three-propylene chains (three-propylene chains arranged with no intervening ethylene units), which are the smallest units for stereoregular structure (for example in the case of three-propylene chain units 1, in the case of four-propylene chain units 2, and in the case of five-propylene chain units 3), namely the number y of the said three-propylene chains which assume the mm arrangement from among the mm arrangement (isotactic arrangement), mr arrangement, and rr arrangement.

As stated above, the microisotacticity seen in the three-propylene chains in the present invention was something which quantitatively determined the percentage of three-propylenes which were arranged isotactically in the said three-propylene chain units; that itself was observed in three-propylene chains by means of a well known ^{13}C -nuclear magnetic resonance spectral technique.

These numerical values were ones smaller than 0.8; for example for materials produced by employing a vanadium catalyst, ordinarily they were ≤ 0.6 , but because copolymers such as these had low softening points and small tensile strengths, they were not desirable.

As long as the various aforementioned properties were not lost to the α -olefin type random copolymers which were obtained by the process of the present invention, it was fine if small amounts of other α -olefin components were copolymerized.

The α -olefin type random copolymers which were obtained by the process of the present invention possessed distinctive characteristics in that they had low contents of low molecular weight components in the whole domain of α -olefin component content by comparison with the α -olefin-ethylene type random copolymers known from the past, were excellent in transparency, were excellent in surface nontackiness, and were excellent in rigidity and other dynamic properties.

The novel α -olefin type random copolymers can be produced by means of copolymerizing ethylene and α -olefins having ≥ 3 for the specified number of carbon atoms in the presence of a catalyst which is formed from

(A) compounds of periodic table group IVB transition metals having as ligands multisite coordination compounds in which at least two kinds of groups which are selected from the group consisting of indenyl groups, substituted indenyl groups, and their partial hydrogenation products are bonded through the medium of lower alkyl groups and

(B) aluminoxanes.

As periodic table group IVB transition metals, titanium, zirconium, and hafnium can be cited. Among them, zirconium is favorable.

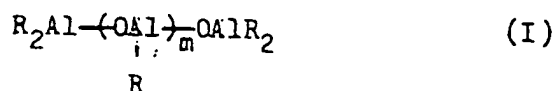
As examples of transition metal compounds in which the transition metal is zirconium which can be employed in the process of the present invention, ethylenebis(indenyl)dimethylzirconium, ethylenebis(indenyl)diethylzirconium, ethylenebis(indenyl)diphenylzirconium, ethylenebis(indenyl)methylzirconium monochloride, ethylenebis(indenyl)ethylzirconium monochloride, ethylenebis(indenyl)methylzirconium monobromide, ethylenebis(indenyl)zirconium dichloride, ethylenebis(indenyl)zirconium dibromide, ethylenebis(4,5,6,7-tetrahydro-1-indenyl)dimethylzirconium, ethylenebis(4,5,6,7-tetrahydro-1-indenyl)methylzirconium monochloride, ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride, ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium dibromide, ethylenebis(4-methyl-1-indenyl)zirconium dichloride, ethylenebis(5-methyl-1-indenyl)zirconium dichloride, ethylenebis(6-methyl-1-indenyl)zirconium dichloride, ethylenebis(7-methyl-1-indenyl)zirconium dichloride, ethylenebis(5-methoxy-1-indenyl)zirconium dichloride, ethylenebis(2,3-dimethyl-1-indenyl)zirconium dichloride, ethylenebis(4,7-dimethyl-1-indenyl)zirconium dichloride, and ethylenebis(1,7-dimethoxy-1-indenyl)zirconium dichloride can be cited.

As examples of transition metal compounds in which the transition metal is titanium which can be employed in the present invention, ethylenebis(indenyl)titanium dichloride and ethylenebis(4,5,6,7-tetrahydro-1-indenyl)titanium dichloride can be cited.

As examples of transition metal compounds in which the transition metal is hafnium which can be employed in the pres-

ent invention, ethylenebis(indenyl)hafnium dichloride and ethylenebis(4,5,6,7-tetrahydro-1-indenyl)hafnium dichloride can be cited.

As the aluminoxane (B) component in the catalyst compositions which are employed in the process of the present invention, concretely organoaluminum compounds which are represented by general Formula I or general Formula II can be illustrative.



(in the formulas R indicates a hydrocarbon group; m indicates an integer ≥ 2 , desirably ≥ 20 , especially desirably ≥ 25). In the said aluminoxanes R is a hydrocarbon group such as a methyl group, ethyl group, propyl group, or butyl group, desirably a methyl group or ethyl group, especially desirably a methyl group; m is an integer ≥ 2 , desirably an integer ≥ 20 , especially desirably an integer from 25 to 100. As the process for production of the said aluminoxanes, for example the following processes can be illustrative.

(1) A process in which a reaction is caused to take place by adding a trialkylaluminum to a suspension in a hydrocarbon medium of a compound containing adsorbed water or a salt containing water of crystallization, for example magnesium chlo-

ride hydrate, copper sulfate hydrate, aluminum sulfate hydrate, and so forth.

(2) A process in which water is caused to interact directly with triethylaluminum in a medium such as benzene, toluene, ethyl ether, or tetrahydrofuran.

Among these processes it is favorable to use Process (I). Furthermore, a small amount of an organometallic component being contained in the said aluminosilane does not effect a change.

In the present invention the thing which was discovered was that copolymers having qualities not proposed in the past are obtained due to producing the copolymers having specified proportions of an α -olefin and ethylene by using catalysts such as described above.

Copolymerization of the α -olefin and ethylene can be carried out in either the liquid phase or the vapor phase, but especially carrying it out in the liquid phase is desirable. In cases where it is carried out in the liquid phase, ordinarily it is put into practice in a hydrocarbon medium. As hydrocarbon media, for example pentane, hexane, heptane, octane, decane, and other aliphatic hydrocarbons, cyclopentane, methylcyclopentane, cyclohexane, cyclooctane, and other alicyclic hydrocarbons, benzene, toluene, xylene, and other aromatic hydrocarbons, and gasoline, kerosene, (illegible) oil, and other petroleum fractions may be cited. Besides these, the olefin starting materials themselves can be used as hydrocarbon media. Among these hydrocarbon media, aromatic hydrocarbons are desirable.

When the process of the present invention is implemented as a liquid-phase polymerization process, the used proportions of the said transition metal compounds as the concentrations of transition metal atoms in the polymerization reaction systems are ordinarily in the range of 10^{-7} to 10^{-2} gram atoms/L, desirably 10^{-6} to 10^{-3} gram atoms/L. And the used proportions of the aluminoxane, as the concentration of aluminum atoms in the polymerization reaction system, are amounts which ordinarily turn out to be in the range of 10^{-4} to 10^{-1} gram atoms/L, desirably 10^{-3} to 5×10^{-2} gram atoms/L; moreover, the ratio of aluminum atoms relative to transition metal atoms in the polymerization reaction system is ordinarily in the range of 20 to 10^4 , desirably 50 to 10^3 .

The copolymerization of the present invention can be conducted ordinarily in the same way as olefin polymerization by employing a Ziegler type catalyst. It is good if the polymerization temperature is usually selected in the range of -80 to 50, desirably -60 to 30. Furthermore, the polymerization can be conducted anyway under ordinary pressure, under pressurization, and under reduced pressure, but conducting it under pressurization is favorable. Ordinarily, it is carried out under a pressure in the range from ordinary pressure to 30 kg/cm^2 , desirably in the range from 2 to 20 kg/cm^2 .

It is desirable for the starting materials which are supplied to the polymerization reaction system to be a mixture consisting of an α -olefin and ethylene. The content of the α -olefin in the polymerization feedstock olefin is ordinarily

in the range of 40 to 99.9 mole%, desirably 50 to 99.8 mole%; the content of ethylene is ordinarily in the range of 0.1 to 60 mole%, desirably 0.2 to 50 mole%. Control of the molecular weight of the copolymer can be accomplished in dependence on hydrogen and/or polymerization temperature and further in dependence on the used proportions of the catalyst components.

The α -olefin type random copolymers which are obtained in the process of the present invention are not tacky and differ from ones proposed in the past from the standpoint of providing various properties other than such as discussed previously. These α -olefin type random copolymers can be molded into pipes, films, sheets, hollow containers, and various other products by means of optional molding processes such as extrusion molding, hollow cavity molding, injection molding, press molding, and vacuum molding and can be supplied for various kinds of uses. Because of being good especially in transparency, resistance to blocking, and heat sealability, they are very suitable as films for packaging use. Due to the aforementioned qualities they can be very suitably used as protective films for metals and so forth.

At the time of molding, various stabilizers, antioxidants, ultraviolet radiation absorbers, antistatic agents, lubricants, plasticizers, pigments, and inorganic or organic fillers can be admixed. As examples of them, it is fine if they are 2,6-di-tert-butyl-p-cresol, tetrakis(methylene-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionato)methane, 4,4'-butylidenebis-

(6-tert-butyl-m-cresol), tocopherols, ascorbic acid, dilauryl thioldipropionate, phosphoric acid type stabilizers, fatty acid monoglycerides, N,N-(bis-2-hydroxyethyl)alkylamines, 2-(2'-hydroxy-3',5'-di-tert-butylphenyl)-5-chlorobenzotriazole, calcium stearate, magnesium oxide, magnesium hydroxide, alumina, aluminum hydroxide, silica, hydrocalcite (misprinted haidorotarusaito?), talc, clay, gypsum, glass fibers, titania, calcium carbonate, carbon black, petroleum resins, polybutene, wax, synthetic or natural rubber, and so forth.

The α -olefin type random copolymers which are obtained according to the process of the present invention can be blended into various kinds of thermoplastic resins as modifiers where those modifiers for example improve the impact resistance, especially the low-temperature impact resistance, flexibility, and low-temperature heat sealability.

By means of blending the α -olefin type random copolymers which are obtained according to the process of the present invention into other ethylene type polymers containing ethylene as the main component such as polyethylene it turns out that the impact strength, low-temperature impact strength, flexibility, and low-temperature heat sealability of molded products of the said other ethylene type polymers can be improved. As the above mentioned other ethylene type polymers, high-density polyethylene, medium-density polyethylene, low-density polyethylene, and ethylene type copolymers and so forth which have been obtained by means of processes other than the process

of the present invention in which ethylene is contained as the main component and which are copolymers of ethylene with C_3-20 - α -olefins such as propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, and 1-eicosane can be illustrative. Limiting viscosities ($[\eta]$) measured at 135 °C in decalin are ordinarily in the range of 0.5 to 20 dL/g.

In cases where the α -olefin type random copolymers which are obtained according to the process of the present invention are blended into the said other ethylene type polymers, the blending proportions are ordinarily in the range of 1 to 100 parts by weight, desirably 2 to 60 parts by weight referred to 100 parts by weight of the said ethylene type polymers. Various kinds of additives, according to need, can be blended into the obtained ethylene type polymer compositions such as antioxidants, hydrochloric acid-absorbing agents, antiagglomeration agents, heat-resisting stabilizers, ultra-violet radiation absorbing agents, lubricants, weather-resisting stabilizers, antistatic agents, nucleating agents, pigments, and fillers. The blending proportions are suitable. The said ethylene type polymer compositions can be produced in accordance with processes known from the past.

By means of blending the α -olefin type random copolymers which are obtained according to the process of the present invention into crystalline olefin type polymers other than the aforementioned other ethylene type polymers, the impact

resistance, especially the low-temperature impact resistance of the compositions formed from the said crystalline olefin type polymers can be improved. Furthermore, films are obtained in which a balance of antiblocking characteristics, transparency, and slip properties is gotten. Concretely, as crystalline olefin type polymers other than the said ethylene type polymers, besides polypropylene, poly-1-butene, poly-4-methyl-1-pentene, and so forth, crystalline α -olefin type copolymers and so forth which are formed from propylene, 1-butene, and 1-hexene and other α -olefins (a_1) as in propylene-ethylene copolymers, propylene-1-butene copolymers, 1-butene-ethylene copolymers, 1-butene-propylene copolymers, and so forth and from α -olefins (a_2) differing from the aforementioned α -olefins (a_1); ethylene, propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, 1-eicosene, and other C_{2-20} - α -olefins can be illustrative. The limiting viscosities (η) measured at 135 °C for the said crystalline olefin type polymers in decalin are in the range of 0.5 to 10 dL/g. The degree of crystallization is $\geq 5\%$, desirably $\geq 20\%$.

In cases where the α -olefin type random copolymers which are obtained according to the process of the present invention are blended into the said crystalline α -olefin type polymers, the blending proportions are ordinarily in the range of 1 to 100 parts by weight, desirably 2 to 60 parts by weight referred to 100 parts by weight of the said crystalline α -olefin type polymer. According to need, various kinds of additives can be blended into the said crystalline α -olefin type polymer

compositions such as antioxidants, hydrochloric acid-absorbing agents, antiagglomeration agents, heat-resisting stabilizers, ultraviolet radiation absorbing agents, lubricants, weather-resisting stabilizers, antistatic agents, nucleating agents, pigments, and fillers. The said crystalline α -olefin type polymer compositions can be produced in accordance with processes known from the past.

Still further, by means of blending the α -olefin type random copolymers which are obtained according to the process of the present invention into various kinds of engineering resins, the properties of the said engineering resins, for example the impact resistance, especially the low-temperature impact resistance, and vibration properties can be improved. In cases where the said engineering resins are engineering resins possessing polar groups, for the purpose of making better the affinity or dispersibility of the said engineering resins, in the olefin type random copolymers which are obtained according to the process of the present invention employment of modified α -olefin type random copolymers which have been graft copolymerized with components of unsaturated carboxylic acids or their derivatives such as maleic acid, citraconic acid, itaconic acid, maleic anhydride, citraconic anhydride, itaconic anhydride, dimethyl maleate, dimethyl citraconate, and dimethyl itaconate is desirable. The proportion of grafts of components of the said unsaturated dicarboxylic acids or their derivatives is ordinarily in the range

of 0.02 to 50 parts by weight referred to 100 parts by weight of the said α -olefin type random copolymers. Concretely, as engineering resins, polyethylene terephthalate, polybutylene terephthalate, and other polyesters, hexamethylene adipamide, octamethylene adipamide, decamethylene adipamide, dodecamethylene adipamide, polycaprolactone (misprint for polycaprolactam?), and other polyamides, polyphenylene oxide and other polyarylene oxides, polyacetals, ABS, AES, polycarbonate, and others can be illustrative. The blending proportions for the said α -olefin type random copolymers or their modification products are ordinarily in the range of 2 to 20 parts by weight referred to 100 parts by weight of the said engineering resin. According to need, various kinds of additives such as antioxidants, hydrochloric acid-absorbing agents, antiagglomeration agents, heat-resisting stabilizers, ultraviolet radiation-absorbing agents, lubricants, weather-resisting stabilizers, antistatic agents, nucleating agents, pigments, and fillers can be mixed into the said engineering resin compositions. The said engineering resin compositions can be produced in accordance with processes known from the past.

The said rubbery polymer properties, for example chemical resistance, rigidity, and so forth can be improved by means of mixing the α -olefin type random copolymers which are obtained according to the process of the present invention into various kinds of rubbery polymers. Concretely, as the said

rubbery polymers, for example ethylene-propylene-nonconjugated diene copolymers, ethylene-1-butene-nonconjugated diene copolymers, polybutadiene rubber, polyisoprene rubber, styrene-butadiene-styrene block copolymers, and so forth can be illustrative. The blending proportions for the said α -olefin type random copolymers are ordinarily in the range of 1-100 parts by weight referred to 100 parts by weight of the aforementioned rubbery polymers. According to need, fillers, crosslinking agents, crosslinking auxiliaries, pigments, stabilizers, and various other kinds of filling agents can be mixed in. The said rubbery polymer compositions can be produced in accordance with processes known from the past.

(Practicable Examples)

Next, the process for production of the α -olefin type random copolymers of the present invention is described concretely by means of practicable examples.

Practicable Example 1

(a) Preparation of ethylenebis(indenyl)zirconium dichloride

After 100 mL of tetrahydrofuran had been transferred into a 500 mL glass flask in which nitrogen had been fully substituted, it was cooled down to -195°C . 8.2 g of zirconium tetrachloride was added to it, and it was brought into the suspended state by means of raising the temperature gradually to room temperature. In succession, 35 mmols of the lithium salt of bis(indenyl)ethane dissolved in 80 mL of tetrahydrofuran was added (ref. J. Organometal. Chem. 232, 233(1982)), and

they were stirred for 2 h at 20 °C. After that and after hydrogen chloride gas had been blown in for several seconds, immediately tetrahydrofuran and hydrogen chloride gas were eliminated under reduced pressure, and a solid was obtained. That solid was washed with 10% hydrochloric acid, water, ethanol, and diethyl ether and was dried under reduced pressure. 4.9 g of ethylenebis(indenyl)zirconium dichloride was obtained.

(b) Preparation of ethylenebis(4,5,6,7-tetrahydro-1-indenyl)-zirconium dichloride

After 4.5 g of the ethylenebis(indenyl)zirconium dichloride which had been synthesized as described above, 300 mg of platinum (IV) oxide, and 100 mL of dichloromethane had been transferred into a 1 L stainless autoclave, hydrogen was introduced and brought to 100 kg/cm² gage. The hydrogenation reaction was conducted at 20 °C for 1 h. After this reaction mixture had been transferred into 1 L of dichloromethane, the platinum(IV) oxide was filtered off, and a solid was obtained by means of removing the dichloromethane. After this solid had been washed with petroleum ether, by means of recrystallizing it from hot toluene, 2.9 g of ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride was obtained.

(c) Preparation of methylaluminoxane

After 70 g of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and 625 mL of toluene had been incorporated into a 2 L glass flask in which argon had been thoroughly substituted and they had been cooled to 0 °C, 1.25

moles of trimethylaluminum diluted with 625 mL of toluene was added dropwise. After the dropwise addition had been terminated, the temperature was raised to 60 °C, and the reaction was conducted at that temperature for 96 h. After the reaction, solid-liquid separation was accomplished by means of filtration, and the separated liquid was used in the polymerization as an aluminoxane solution. On removing toluene from one portion of the separated liquid it was taken as a sample for use in molecular weight determination. The molecular weight found from the depression of the freezing point in benzene was 1570. The n value for the said aluminoxane was 25.

(d) Polymerization

20 L of purified toluene, 10 kg (238 moles) of propylene, and 2.9 kg (104 moles) of ethylene were transferred at -15 °C into a stainless autoclave of 100 L internal capacity in which nitrogen had been thoroughly substituted; in succession, methylaluminoxane corresponding to 0.4 gram atoms on conversion to aluminum atoms and ethylenebis(4,5,6,7-tetrahydro-1-indenyl)-zirconium dichloride corresponding to 0.4 milligram atoms on conversion to zirconium atoms were incorporated; the polymerization was conducted at -15 °C for 5 h. The polymerization was terminated by means of adding a small quantity of methanol, and the unreacted propylene and ethylene were purged. Furthermore, after catalyst residues had been removed by means of hot water to which a small quantity of hydrochloric acid and

methanol had been added, the polymer was precipitated by dumping the liquid polymerization mixture into a large quantity of methanol. After the precipitated polymer had been washed with more methanol, it was dried at 100 °C under reduced pressure for one day and night. 1230 g of the copolymer made in this way was obtained. The ethylene content in the copolymer measured by means of ^{13}C -NMR was 41.8 mole%; the limiting viscosity (η) found in decalin at 135 °C was 2.80 dL/g; M_w/M_n found from GPC was 2.42; the DSC melting point was 64 °C; the degree of crystallization measured by an x-ray diffraction method was 0.9%; and the B value found from ^{13}C -NMR was 1.26. Additionally, the fraction soluble in boiling methyl acetate was 0.04 wt%; the fraction soluble in acetone-n-decane mixed solvent was 0.22 wt%; the stress at the breaking point was 10 kg/cm²; the elongation at the breaking point was 1100%; the JIS A hardness was 45; the haze was 9%; and the microisotacticity found by the ^{13}C -NMR was 0.95. In the ^{13}C -NMR spectrum for the obtained copolymer, $\alpha\beta$ and $\beta\gamma$ signals attributable to methylene chains between two neighboring tertiary carbon atoms were not observed.

Practicable Examples 2-8, Comparison Examples 2,3

The polymerizations were conducted in the same way as in Practicable Example 1 except that the kinds and proportions of the monomers which were supplied for polymerization in Practicable Example 1 and the polymerization temperatures and polymerization times were changed. In the ^{13}C -NMR spectra

of the obtained copolymers, $\alpha\beta$ and $\beta\gamma$ signals attributable to methylene chains between two adjacent tertiary carbon atoms were not observed. The polymerization results are shown in Table 1.

Practicable Example 9

The polymerization was conducted in the same way as in Practicable Example 1 except that 0.45 milligram atoms converted to zirconium atoms was used for the ethylenebis(indenyl)zirconium dichloride which had been synthesized in the same way as in Practicable Example 1 and the polymerization time was taken as 10 h. In the ^{13}C -NMR spectrum for the obtained copolymer, $\alpha\beta$ and $\beta\gamma$ signals attributable to methylene chains between two neighboring tertiary carbon atoms were not observed.

The polymerization results are shown in Table 1.

Practicable Example 10

The polymerization was conducted in the same way as for Practicable Example 5 except that 0.45 milligram atoms converted to zirconium atoms was used for the ethylenebis(indenyl)zirconium dichloride and that the polymerization time was taken as 30 h. In the ^{13}C -NMR spectrum for the obtained copolymer, $\alpha\beta$ and $\beta\gamma$ signals attributable to methylene chains between two adjacent tertiary carbon atoms were not observed.

Comparison Example 1

Preparation of the titanium catalyst

20 g of commercial anhydrous magnesium chloride, 4.5 mL of ethyl benzoate, and 3.0 mL of methyl polysiloxane were in-

corporated under a nitrogen atmosphere in a stainless pot of 800 mL internal capacity in which 2.8 kg of stainless balls were accommodated (?), and they were contact-pulverized for 12 h at an impact acceleration of 7G. Then, 10 g of the obtained true solid product was suspended in 100 mL of titanium tetrachloride, and they were caused to react at 80 °C for 2 h. After the termination of the reaction, filtration was carried out, and the obtained solid portion was washed thoroughly with hexane. In this way a titanium catalyst containing 2.0 wt% titanium and 6.5 wt% ethyl benzoate was obtained.

Polymerization

30 L of purified decane was charged into a stainless autoclave of 100 L internal capacity in which nitrogen had been thoroughly substituted; after a propylene-ethylene gas mixture (propylene/ethylene molar ratio, 75/25) at a flow rate of 19 kg/h and hydrogen at a flow rate of 80 L/h had been allowed to flow through and the temperature had been raised to 60 °C, 25 milligram atoms converted to aluminum atoms of triethylaluminum, 8.5 millimoles of methyl p-toluate, and 0.5 milligram atoms converted to titanium atoms of the previously described titanium catalyst were incorporated; the polymerization was initiated; and the polymerization was conducted for 15 min. After that, the operations were carried out in the same way as in Practicable Example 1. In this way 1450 g of copolymer was obtained. The results are shown in Table 1.

Comparison Example 4

5 kg (89 moles) of 1-butene, 40 g (1.4 moles) of ethylene, and 2.3 g (1.2 moles) of hydrogen were incorporated at room temperature into a stainless autoclave of 20 L internal capacity; in succession, diethylaluminum chloride corresponding to 20 milligram atoms converted to aluminum atoms and titanium trichloride corresponding to 10 milligram atoms converted to titanium atoms (Toho Titanium brand TAC-131) were incorporated; and the polymerization was initiated. The polymerization was conducted for 1 h at 70 °C. After that, the operations were carried out in the same way as in Practicable Example 1. In this way 750 g of copolymer was obtained. The results are shown in Table 1.

Key for Table 1

- 1) Practicable Examples
- 2) Comparison Examples
- 3) α -Olefin (variety)
- 4) Propylene
- 5) 1-Butene
- 6) Supplied monomer, α -olefin*/ethylene (molar ratio)
- 7) Polymerization temperature (°C)
- 8) Polymerization time (hr)
- 9) Copolymer yield (g)
- 10) Ethylene content (mole%)
- 11) Limiting viscosity (η) (dL/g)

- 12) \bar{M}_w/\bar{M}_n
- 13) Melting point ($^{\circ}\text{C}$)
- 14) Degree of crystallization (%)
- 15) B value
- 16) Fraction soluble in boiling methyl acetate (wt%)
- 17) Fraction soluble in acetone-n-decane (wt%)
- 18) Stress at the breaking point (kg/cm^2)
- 19) Elongation at the breaking point (%)
- 20) Shear stress at the yield point (kg/cm^2)
- 21) Torsional rigidity modulus (kg/cm^2)
- 22) Young's modulus (kg/cm^2)
- 23) Hardness JIS A
- 24) Haze (%)
- 25) Microisotacticity
- 26) Standard deviation (mole%)
- 27) * -Olefin copolymerization, 10 kg

(but with the exception of Comparison Examples 1, 4)

(Some characters in this machine-copied Japanese Kokai patent were virtually illegible, so educated guesses were required for translation of a few of them.)

Table 1

| Example | | monomer | α -olefin* / ethylene (molar ratio) | polymerization temperature (°C) | polymerization time (hr) | yield amount (g) | ethylene content (mole %) | intrinsic viscosity $[\eta]$ (dl/g) | \bar{M}_w/\bar{M}_n |
|---------------------|----|----------------------------|---|---------------------------------|--------------------------|------------------|---------------------------|-------------------------------------|-----------------------|
| | | α -olefin (kind) | | | | | | | |
| Example | 1 | propylene | | | | | | | |
| | 2 | ditto | | | | | | | |
| | 3 | ditto | | | | | | | |
| | 4 | ditto | | | | | | | |
| | 5 | 1-butene | | | | | | | |
| | 6 | ditto | | | | | | | |
| | 7 | ditto | | | | | | | |
| | 8 | ditto | | | | | | | |
| | 9 | propylene | | | | | | | |
| | 10 | 1-butene | | | | | | | |
| Comparative Example | 1 | propylene | | | | | | | |
| | 2 | 1-butene | | | | | | | |
| | 3 | ditto | | | | | | | |
| | 4 | ditto | | | | | | | |

| | α -olefin (種別) | α -olefin* / エチレン (モル比) | 重合温度 (°C) | 重合時間 (hr) | 重合率 (%) | エチレン含有率 (モル%) | 重合度 (dl/g) | \bar{M}_w/\bar{M}_n |
|------|-----------------------|--------------------------------|-----------|-----------|---------|---------------|------------|-----------------------|
| 例1 | プロピレン | 70/30 | -15 | 5 | 1230 | 4.18 | 280 | 242 |
| 2 | " | 75/25 | " | " | 1150 | 3.49 | 251 | 235 |
| 3 | " | 80/20 | -10 | " | 1070 | 3.13 | 227 | 240 |
| 4 | " | 85/15 | " | " | 980 | 2.50 | 216 | 229 |
| 5 | 1-ブテン | 90/10 | -20 | 15 | 610 | 1.82 | 232 | 231 |
| 6 | " | 95/5 | " | 20 | 660 | 1.5 | 215 | 220 |
| 7 | " | 98/2 | " | " | 590 | 1.9 | 198 | 218 |
| 8 | " | 80/20 | -15 | 10 | 720 | 3.33 | 206 | 241 |
| 9 | プロピレン | 70/30 | " | " | 1100 | 4.02 | 276 | 245 |
| 10 | 1-ブテン | 90/10 | -20 | 30 | 640 | 2.02 | 224 | 236 |
| 比較例1 | プロピレン | 75/25 | -40 | 0.25 | 1450 | 3.97 | 279 | 457 |
| 2 | 1-ブテン | 99.8/0.2 | -20 | 20 | 550 | 0.5 | 181 | 221 |
| 3 | " | 45/55 | -10 | 6 | 680 | 3.94 | 252 | 239 |
| 4 | " | 98/2 | 70 | 1 | 750 | 7.8 | 265 | 695 |

Table 1 (continued)

Example 1

Comparative
Example 1

| | melting point (°C) | degree of crystallization (%) | B-value | soluble fraction in boiling methyl acetate (% by weight) | soluble fraction in acetone-n-decane (% by weight) | stress at break (kg/cm ²) | elongation at break (%) | stress at yield point (kg/cm ²) |
|-------|--------------------|-------------------------------|---------|--|--|---------------------------------------|-------------------------|---|
| | 融点 (°C) | 結晶度 (%) | B 値 | 沸騰メチルアセテート 可溶成分 (重量%) | アセトン・ノルデセン 可溶成分 (重量%) | 破断力 (kg/cm ²) | 破断伸び (%) | 破断点 (kg/cm ²) |
| 実施例 1 | 64 | 0.9 | 1.24 | 0.04 | 0.22 | 10 | 1100 | - |
| 2 | 73 | 12 | 1.23 | 0.04 | 0.23 | 60 | 980 | - |
| 3 | 84 | 24 | 1.21 | 0.07 | 0.30 | 135 | 900 | - |
| 4 | 102 | 45 | 1.20 | 0.07 | 0.34 | 230 | 820 | - |
| 5 | 91 | 14 | 1.16 | 0.03 | 0.40 | 140 | 710 | 30 |
| 6 | 101 | 25 | 1.10 | 0.02 | 0.31 | 300 | 660 | 65 |
| 7 | 107 | 40 | 1.04 | 0.02 | 0.10 | 510 | 400 | 120 |
| 8 | 75 | 4 | 1.26 | 0.05 | 0.39 | 40 | 700 | 10 |
| 9 | 68 | 10 | 1.25 | 0.04 | 0.21 | 15 | 1050 | - |
| 10 | 90 | 12 | 1.19 | 0.03 | 0.42 | 120 | 750 | 25 |
| 比較例 1 | 116.70 | 31 | 0.79 | 0.59 | 1.79 | 10 | 1200 | - |
| 2 | 122 | 54 | 1.00 | 0.02 | 0.12 | 500 | 380 | 180 |
| 3 | 23 | 0.5 | 1.27 | 0.30 | 0.71 | 4 | 770 | 4 |
| 4 | 98 | 35 | 0.78 | 2.51 | 2.21 | 120 | 580 | 20 |

Table 1 (continued)

Example 1

Comparative
Example 1

| | ねじり剛性係数 (n/d) | ヤング率 (n/d) | JIS A 硬度 | haze (%) | microisotacticity | 標準偏差 (mole %) |
|-------|------------------|---------------|-------------|----------|-------------------|---------------|
| 実施例 1 | — | — | 45 | 9 | 0.95 | — |
| 2 | — | — | 49 | 10 | 0.94 | — |
| 3 | — | — | 81 | 10 | 0.96 | — |
| 4 | — | — | 95 | 12 | 0.94 | — |
| 5 | 210 | 500 | — | — | — | 15 |
| 6 | 420 | 1100 | — | — | — | 25 |
| 7 | 870 | 1900 | — | — | — | 23 |
| 8 | 30 | 100 | — | — | — | 21 |
| 9 | — | — | 60 | 9 | 0.95 | — |
| 10 | 150 | 400 | — | — | — | 17 |
| 比較例 1 | — | — | 62 | 25 | 0.82 | — |
| 2 | 1250 | 2900 | — | — | — | 21 |
| 3 | 5 | 15 | — | — | — | 38 |
| 4 | 90 | 200 | — | — | — | 57 |

α-オレフィンの量
1.0 kg
(ただし比較例 1, 4 を除く)

* amount of charged α-olefin 10 kg
(with exceptions of Comparative
Examples 1 and 4)

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